

CONTROLLING TEMPERATURE AND PRESSURE IN MD

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DIPARTIMENTO DI FISICA



SAPIENZA
UNIVERSITÀ DI ROMA

OUTLINE

- Complements in MD
- Thermostats and barostats
- bibliography

NOTES ON INTEGRATORS

Frenkel & Smit Understanding Molecular Simulations 4.2,
Schiller2008

An interesting course David Ceperley from which we shall
present a few slides, as such.

<https://courses.physics.illinois.edu/phys466/fa2018/>

Elegant lectures by Michiel Sprik

Introduction to molecular dynamics methods

(see Binder_Ciccotti1996.pdf)

Elegant,rigorous and compact lectures by Michiel Sprik

Introduction to molecular dynamics methods

Chap.3 in “Montecarlo and Molecular Dynamics of Condensed Matter Systems (K. Binder and G. Ciccotti Eds.)SIF, Bologna, 1996)

- **Basic Molecular Dynamics** (Newton’s equations of motion, Criteria for time iteration in MD, Verlet algorithm)
- **Dynamics in Phase Space** (Hamiltonian dynamics, Liouville operators, Factorization of phase space propagators)
- **MD under Constant Pressure and Temperature** (Equilibrium statistical mechanics, Instantaneous temperature and pressure, [kinetic temperature, instantaneous virial pressure], Constant pressure MD [Andersen’s algorithm], Constant temperature MD [Nosé-Hoover dynamics])
- **Multiple Time Scales** (Constraint dynamics[Ciccotti-Ryckaert,1987], Multiple time steps[Tuckerman, Martyna and Berne 1992])
- **Long Range Interactions** (Dielectrics, reaction field method, Ewald summation, Polarization fluctuations and dielectrics)
- **Free Energy and Rare Events** (potential of mean force and reversible work, [this is still an active field])

THE OPERATOR ORIGIN OF VELOCITY VERLET

384

Brazilian Journal of Physics, vol. 34, no. 2A, June, 2004

Symplectic Integration Methods in Molecular and Spin Dynamics Simulations

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We review recently developed decomposition algorithms for molecular dynamics and spin dynamics simulations of many-body systems. These methods are time reversible, symplectic, and the error in the total energy thus generated is bounded. In general, these techniques are accurate for much larger time steps than more standard integration methods. Illustrations of decomposition algorithms performance are shown for spin dynamics simulations of a Heisenberg ferromagnet.

2 Molecular Dynamics

Let us consider a system of N particles with masses m_i described by their positions \mathbf{r}_i and velocities \mathbf{v}_i , interacting via a potential $u(r_{ij})$, where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The Hamiltonian function of the system can be written as

$$\mathcal{H} = \sum_{i=1}^N \frac{1}{2} m_i v_i^2 + \sum_{i,j, j \neq i} u(r_{ij}), \quad (1)$$

and the force on particle i due to particle j is given by

$$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} u(r_{ij}) = -\frac{\partial u(r_{ij})}{\partial r_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}}. \quad (2)$$

The equations of motion are given by

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j, j \neq i} \mathbf{f}_{ij} \equiv \mathbf{f}_i, \quad i = 1, \dots, N. \quad (3)$$

The time evolution of the system can be studied by integrating the equations of motion to obtain $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$, for $i = 1, 2, \dots, N$, and by expressing other physical quantities in terms of $\mathbf{r}_i(t)$ and $\mathbf{v}_i(t)$.

2.1 Liouville Formulation

The equations of motion (3) can be rewritten as

$$\frac{dy}{dt} = \hat{L}y(t) \quad (4)$$

where $y(t) = \{\mathbf{r}_i(t), \mathbf{v}_i(t)\}$ denotes a configuration of the N particles, and \hat{L} is the Liouville operator defined as

$$\hat{L} \equiv \sum_{i=1}^N \left(\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + \frac{\mathbf{f}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{v}_i} \right) \equiv A + B \quad (5)$$

The term $\sum_{i=1}^N \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \equiv A$ in Eq.(5) corresponds to the free motion of the particles (kinetic part), whereas the potential part is given by the term $\sum_{i=1}^N \frac{\mathbf{f}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{v}_i} \equiv B$. With these definitions of operators A and B , the equations of motion (4) can be written as

$$\frac{dy}{dt} = (A + B)y(t), \quad (6)$$

which have the formal solution

$$y(t + \Delta) = e^{(A+B)\Delta} y(t), \quad (7)$$

where Δ represents a time step. For a general many-body system the combined operation $e^{(A+B)\Delta} y(t)$ cannot be easily performed. However, the separate operators $e^{A\Delta} y$ and $e^{B\Delta} y$ can be written as

$$e^{A\Delta} y = \exp \left(\Delta \sum_{i=1}^N \mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \right) \{\mathbf{r}_i, \mathbf{v}_i\} = \{\mathbf{r}_i + \mathbf{v}_i \Delta, \mathbf{v}_i\} \quad (8)$$

$$e^{B\Delta} y = \exp \left(\Delta \sum_{i=1}^N \frac{\mathbf{f}_i}{m_i} \cdot \frac{\partial}{\partial \mathbf{v}_i} \right) \{\mathbf{r}_i, \mathbf{v}_i\} = \{\mathbf{r}_i, \mathbf{v}_i + \frac{\mathbf{f}_i}{m_i} \Delta\} \quad (9)$$

and they represent shifts in the positions and in the velocities, respectively. Moreover, the shift in the positions (velocities) generated by $e^{A\Delta} y$ ($e^{B\Delta} y$) only depends on the velocities (positions) and can be easily computed. However, note that in general $e^{(A+B)\Delta} \neq e^{A\Delta} e^{B\Delta}$!

5.3 Velocity-Verlet algorithm

Another implementation of the Verlet algorithm, denoted as velocity-Verlet algorithm, computes the time evolution of the position and velocity with

$$r(t + \Delta) = r(t) + v(t)\Delta + \frac{f(t)}{2m}\Delta^2 \quad (26)$$

and

$$v(t + \Delta) = v(t) + \frac{f(t + \Delta) + f(t)}{2m}\Delta, \quad (27)$$

respectively. This corresponds to first computing $r(t + \Delta)$ using Eq.(26), then from these new positions the forces $f(t + \Delta)$ can be determined. Finally, the velocities $v(t + \Delta)$ are computed from Eq.(27).

To show the equivalence between the position- and the velocity-Verlet algorithms, we write Eq.(26) for time $t + 2\Delta$, namely

$$r(t + 2\Delta) = r(t + \Delta) + v(t + \Delta)\Delta + \frac{f(t + \Delta)}{2m}\Delta^2, \quad (28)$$

and we then subtract Eq.(26) from Eq.(28) to obtain

$$\begin{aligned} r(t + 2\Delta) - r(t + \Delta) &= v(t + \Delta)\Delta + \frac{f(t + \Delta)}{2m}\Delta^2 \\ &- \left[v(t)\Delta + \frac{f(t)}{2m}\Delta^2 \right] \end{aligned} \quad (29)$$

Substituting Eq.(27) in Eq.(29), we get

$$r(t + 2\Delta) = 2r(t + \Delta) - r(t) + \frac{f(t + \Delta)}{m}\Delta^2 \quad (30)$$

which is the position-Verlet algorithm derived before.

where we have used the shorthand notation \mathbf{r} for \mathbf{r}^N and \mathbf{p} for \mathbf{p}^N . The last line of equation (4.3.8) defines the *Liouville operator*

$$iL = \dot{\mathbf{r}} \frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{p}} \frac{\partial}{\partial \mathbf{p}}. \quad (4.3.9)$$

We can formally integrate equation (4.3.8) to obtain

$$f[\mathbf{p}^N(t), \mathbf{r}^N(t)] = \exp(iLt) f[\mathbf{p}^N(0), \mathbf{r}^N(0)]. \quad (4.3.10)$$

In all cases of practical interest, we cannot do much with this formal solution, because evaluating the right-hand side is still equivalent to the exact integration of the classical equations of motion. However, in a few simple cases the formal solution is known explicitly. In particular, suppose that our Liouville operator contained only the first term on the right-hand side of equation (4.3.9). We denote this part of iL by iL_r :

$$iL_r \equiv \dot{\mathbf{r}}(0) \frac{\partial}{\partial \mathbf{r}}, \quad (4.3.11)$$

where $\dot{\mathbf{r}}(0)$ is the value of $\dot{\mathbf{r}}$ at time $t = 0$. If we insert iL_r in equation (4.3.10) and use a Taylor expansion of the exponential on the right-hand side, we get

$$\begin{aligned} f(t) &= f(0) + iL_r t f(0) + \frac{(iL_r t)^2}{2!} f(0) + \dots \\ &= \exp\left(\dot{\mathbf{r}}(0)t \frac{\partial}{\partial \mathbf{r}}\right) f(0) \\ &= \sum_{n=0}^{\infty} \frac{(\dot{\mathbf{r}}(0)t)^n}{n!} \frac{\partial^n}{\partial \mathbf{r}^n} f(0) \\ &= f[\mathbf{p}^N(0), (\mathbf{r} + \dot{\mathbf{r}}(0)t)^N]. \end{aligned} \quad (4.3.12)$$

Hence, the effect of $\exp(iL_r t)$ is a simple shift of coordinates. Similarly, the effect of $\exp(iL_p t)$, with iL_p defined as

$$iL_p \equiv \dot{\mathbf{p}}(0) \frac{\partial}{\partial \mathbf{p}}, \quad (4.3.13)$$

is a simple shift of momenta. The total Liouville operator, iL , is equal to $iL_r + iL_p$. Unfortunately, we cannot replace $\exp(iLt)$ by $\exp(iL_r t) \times \exp(iL_p t)$,

Velocity Verlet from operator factorization

because iL_r and iL_p are noncommuting operators. For noncommuting operators A and B , we have

$$\exp(A + B) \neq \exp(A) \exp(B). \quad (4.3.14)$$

However, we do have the following *Trotter identity*:

$$e^{(A+B)} = \lim_{P \rightarrow \infty} \left(e^{A/2P} e^{B/P} e^{A/2P} \right)^P. \quad (4.3.15)$$

In the limit $P \rightarrow \infty$, this relation is formally correct, but of limited practical value. However, for large but finite P , we have

$$e^{(A+B)} = \left(e^{A/2P} e^{B/P} e^{A/2P} \right)^P e^{\mathcal{O}(1/P^2)}. \quad (4.3.16)$$

Now let us apply this expression to the formal solution of the Liouville equation. To this end, we make the identification

$$\frac{A}{P} \equiv \frac{iL_p t}{P} \equiv \Delta t \dot{\mathbf{p}}(0) \frac{\partial}{\partial \mathbf{p}}$$

and

$$\frac{B}{P} \equiv \frac{iL_r t}{P} \equiv \Delta t \dot{\mathbf{r}}(0) \frac{\partial}{\partial \mathbf{r}},$$

where $\Delta t = t/P$. The idea is now to replace the formal solution of the Liouville equation by the discretized version, equation (4.3.16). In this scheme, one time step corresponds to applying the operator

$$e^{iL_p \Delta t/2} e^{iL_r \Delta t} e^{iL_p \Delta t/2}$$

once. Let us see what the effect is of this operator on the coordinates and momenta of the particles. First, we apply $\exp(iL_p \Delta t/2)$ to f and obtain

$$e^{iL_p \Delta t/2} f[\mathbf{p}^N(0), \mathbf{r}^N(0)] = f \left\{ \left[\mathbf{p}(0) + \frac{\Delta t}{2} \dot{\mathbf{p}}(0) \right]^N, \mathbf{r}^N(0) \right\}.$$

Next, we apply $\exp(iL_r \Delta t)$ to the result of the previous step

$$\begin{aligned} & e^{iL_r \Delta t} f \left\{ \left[\mathbf{p}(0) + \frac{\Delta t}{2} \dot{\mathbf{p}}(0) \right]^N, \mathbf{r}^N(0) \right\} \\ &= f \left\{ \left[\mathbf{p}(0) + \frac{\Delta t}{2} \dot{\mathbf{p}}(0) \right]^N, [\mathbf{r}(0) + \Delta t \dot{\mathbf{r}}(\Delta t/2)]^N \right\}, \end{aligned}$$

and finally we apply $\exp(iL_p\Delta t/2)$ once more, to obtain

$$f \left\{ \left[\mathbf{p}(0) + \frac{\Delta t}{2} \dot{\mathbf{p}}(0) + \frac{\Delta t}{2} \dot{\mathbf{p}}(\Delta t) \right]^N, [\mathbf{r}(0) + \Delta t \dot{\mathbf{r}}(\Delta t/2)]^N \right\}.$$

Note that every step in the preceding sequence corresponds to a simple shift operation in either \mathbf{r}^N or \mathbf{p}^N . It is of particular importance to note that the shift in \mathbf{r} is a function of \mathbf{p} only (because $\dot{\mathbf{r}} = \mathbf{p}/m$), while the shift in \mathbf{p} is a function of \mathbf{r} only (because $\dot{\mathbf{p}} = \mathbf{F}(\mathbf{r}^N)$). The Jacobian of the transformation from $\{\mathbf{p}^N(0), \mathbf{r}^N(0)\}$ to $\{\mathbf{p}^N(\Delta t), \mathbf{r}^N(\Delta t)\}$ is simply the product of the Jacobians of the three elementary transformations. But, as each of these Jacobians is equal to 1, the overall Jacobian is also equal to 1. In other words, the algorithm is area preserving.

If we now consider the overall effect of this sequence of operations on the positions and momenta, we find the following:

$$\mathbf{p}(0) \rightarrow \mathbf{p}(0) + \frac{\Delta t}{2} (\mathbf{F}(0) + \mathbf{F}(\Delta t)) \quad (4.3.17)$$

$$\begin{aligned} \mathbf{r}(0) &\rightarrow \mathbf{r}(0) + \Delta t \dot{\mathbf{r}}(\Delta t/2) \\ &= \mathbf{r}(0) + \Delta t \dot{\mathbf{r}}(0) + \frac{\Delta^2 t}{2m} \mathbf{F}(0). \end{aligned} \quad (4.3.18)$$

But these are precisely the equations of the Verlet algorithm (in the velocity form). Hence, we have shown that the Verlet algorithm is area preserving. That it is reversible follows directly from the fact that past and future coordinates enter symmetrically in the algorithm.

Finally, let us try to understand the absence of long-term energy drift in the Verlet algorithm. When we use the Verlet algorithm, we replace the true Liouville operator $\exp(iL_t)$ by $\exp(iL_r\Delta t/2) \exp(iL_p\Delta t) \exp(iL_r\Delta t/2)$. In doing so, we make an error. If all (n th-order) commutators of L_p and L_r exist (i.e., if the Hamiltonian is an infinitely differentiable function of \mathbf{p}^N and \mathbf{r}^N) then, at least in principle, we can evaluate the error that is involved in this replacement:

$$\exp(iL_r\Delta t/2) \exp(iL_p\Delta t) \exp(iL_r\Delta t/2) = \exp(iL\Delta t + \epsilon), \quad (4.3.19)$$

where ϵ is an operator that can be expressed in terms of the commutators of L_p and L_r :

$$\epsilon = \sum_{n=1}^{\infty} (\Delta t)^{2n+1} c_{2n+1}, \quad (4.3.20)$$

where c_m denotes a combination of m th-order commutators. For instance, the leading term is

$$-(\Delta t)^3 \left(\frac{1}{24} [iL_r, [iL_r, iL_p]] + \frac{1}{12} [iL_p, [iL_r, iL_p]] \right).$$

Temperature and Pressure Controls

Ensembles

1. (E, V, N) microcanonical (constant energy)
2. (T, V, N) canonical, constant volume
3. (T, P, N) constant pressure
4. (T, V, μ) grand canonical

- #2, 3 or 4 are often better for macroscopic properties
- Today we will learn how we can do #2 and #3 with MD.
- Reading Lesar Section 6.4

Constant Temperature MD

- Problem in MD is *to control the temperature*.
- How to start the system?

Sample the velocities from a Maxwellian (Gaussian) distribution. (we will learn how to do this next time)

$$P(v) = C e^{-\frac{mv^2}{k_B T}} dv$$

- If we start from a perfect lattice as the system becomes disordered, it will suck up the kinetic energy and cool down.
- Vice versa for starting from a gas.
- **QUENCH** method.
- Andersen Thermostat
- Nose-Hoover Thermostat

Quench method (Berendsen)

- Run for a while, *compute kinetic energy*, then *rescale the momentum to correct temperature T* , repeat as needed.

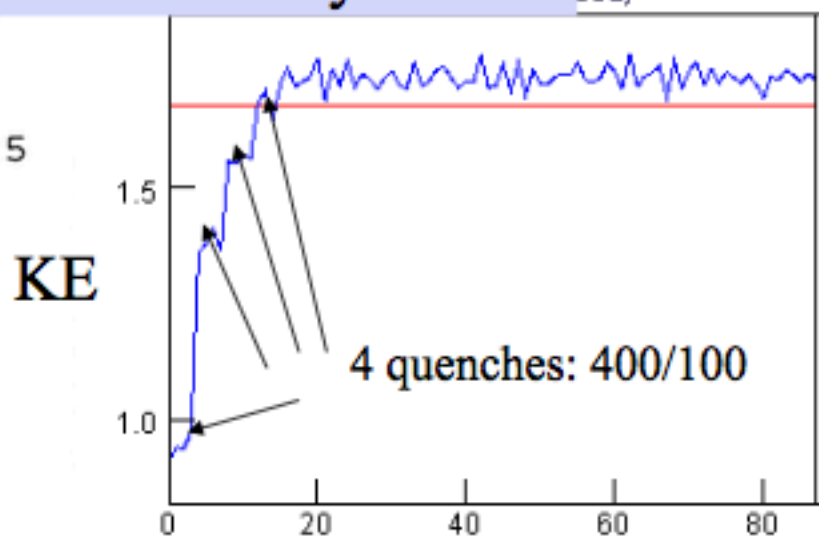
$$k_B T_I = \frac{\sum_i m_i v_i^2}{3N-3} \quad v_i^{new} = \sqrt{\frac{T}{T_I}} v_i^{old} \quad \text{Instantaneous } T_I$$

- Control is at best $O(1/N)$, not real-time dynamics.

```

DIMENSION 3
TYPE argon 256 48.
POTENTIAL argon argon 1 1. 1. 2.5
DENSITY 1.05
TEMPERATURE 1.15
TABLE LENGTH 10000
LATTICE 4 4 4 4
SEED 10
WRITE SCALARS 25
WRITE COORD 25
QUENCH 100
RUN MD 400 .05
QUENCH 0
RUN MD 1800 .05
    
```

2 — 4
 8 — 16
 2 — 72



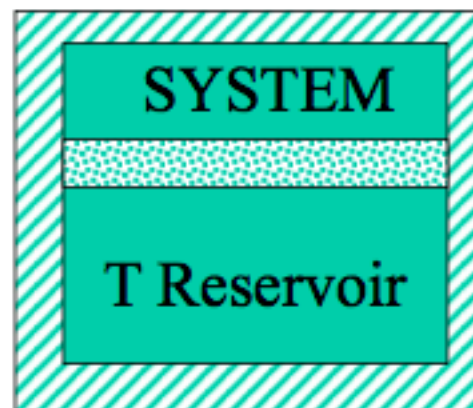
Brownian dynamics/Andersen thermostat

- *Put a system in contact with a heat bath*
- Leads to discontinuous velocities.
- Not necessarily a bad thing, but requires some physical insight into how the bath interacts with the system.
 - For example, this is appropriate for a large molecule (protein or colloid) in contact with a solvent.
 - Other heat baths in nature are given by phonons, photons,...
- We will discuss Brownian dynamics later in the course.
- Andersen thermostat:
 - With some probability, resample velocities from a Maxwell dist. (see FS 6.1.1)

Nose-Hoover thermostat (FS 6.1.2)

- MD in canonical distribution (T,V,N)
- Introduce a *friction* force $\zeta(t)$

$$\frac{dp}{dt} = F(q,t) - \zeta(t)p(t)$$



Dynamics of friction coefficient to get canonical ensemble.

$$Q \frac{d\zeta}{dt} = \sum \frac{1}{2} m_i v_i^2 - \frac{3N}{2} k_B T$$

Feedback makes
K.E.=3/2 kT

$$\frac{d\zeta}{dt} = 0$$

Dynamics at steady-state

Q= fictitious “heat bath mass”. Large Q is weak coupling

Nose-Hoover thermodynamics

- *Energy of physical system fluctuates.* However *energy of system plus heat bath is conserved.*

$$H' = H + \frac{Q}{2} \zeta^2 + g k_B T \ln(s) \quad \text{and} \quad \frac{d \ln(s)}{dt} = \zeta$$

- Derive equation of motion from this Hamiltonian.
 - $dr/dt=p$, $dp/dt= F - p_\zeta/Q$, $d\zeta/dt=p_\zeta/Q$ etc. (see text)
- Hopefully system is *ergodic*.

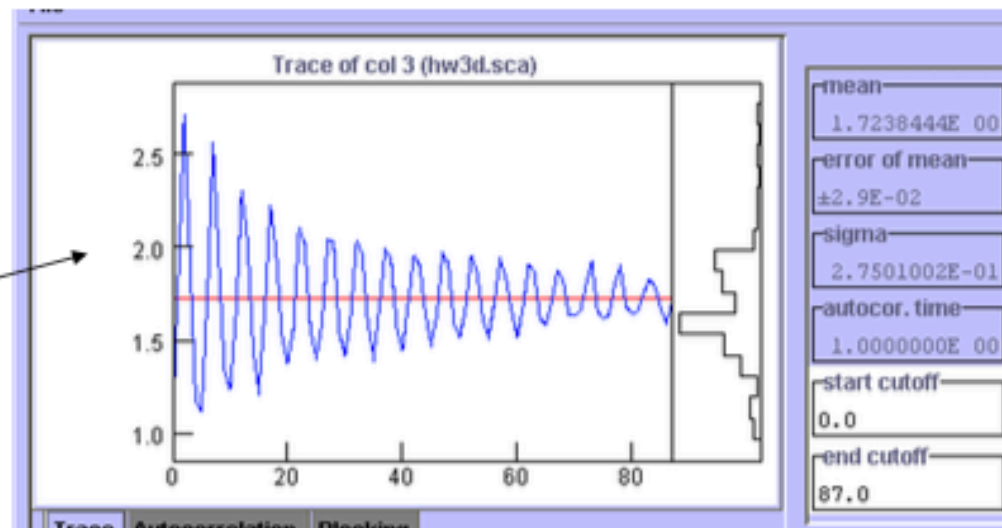
Then stationary state is canonical distribution

$$\exp[-\beta(V + \frac{1}{2m} p^2 + \frac{Q}{2} \zeta^2)]$$

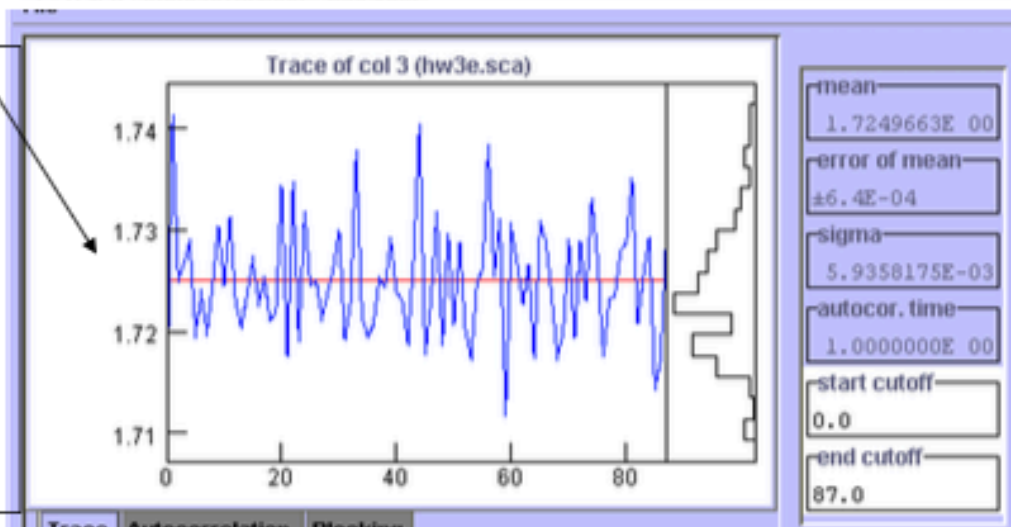
Effect of thermostat

System T fluctuates but
how quickly?

Q=1



Q=100



```
DIMENSION 3
TYPE argon 256 48.
POTENTIAL argon argon 1 1. 1. 2.5
DENSITY 1.05
TEMPERATURE 1.15
TABLE_LENGTH 10000
LATTICE 4 4 4 4
SEED 10
WRITE_SCALARS 25
NOSE 100.
RUN MD 2200 .05
```

- *Thermostats are needed in non-equilibrium situations* where there might be a flux of energy in/out of the system.
- It is *time-reversible, deterministic* and goes to the *canonical distribution* but:
- **How natural is the thermostat?**
 - *Interactions are non-local.* They propagate instantaneously
 - **Interaction with a single heat-bath variable-dynamics can be strange.** Be careful to adjust the “mass”

REFERENCES FS 6.1.2

1. S. Nose, *J. Chem. Phys.* 81, 511 (1984); *Mol. Phys.* 52, 255 (1984).
2. W. Hoover, *Phys. Rev. A* 31, 1695 (1985).

Comparison of Thermostats

Nose-Hoover (*deterministic*) vs. Andersen (*stochastic*)

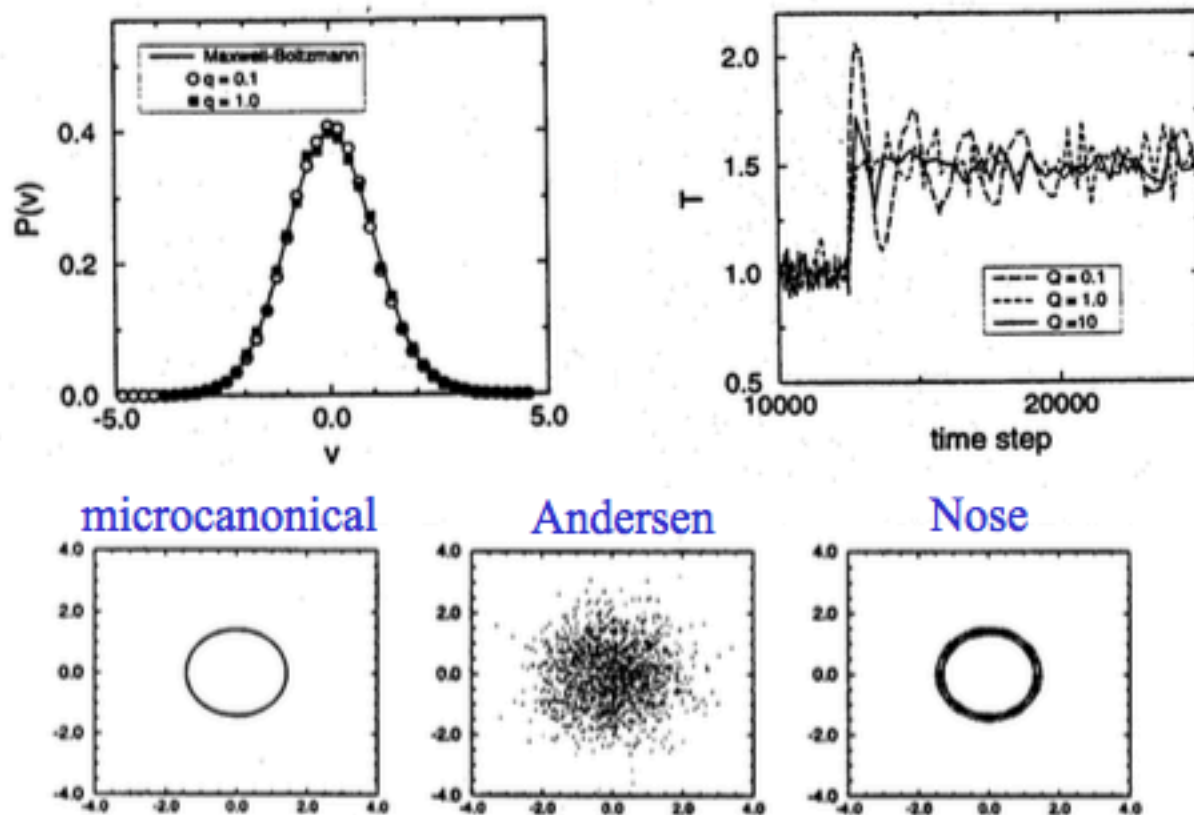
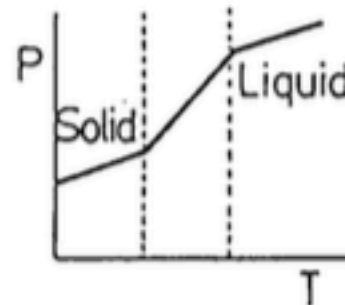
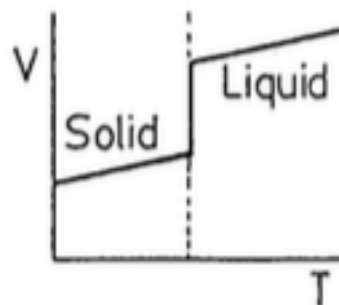
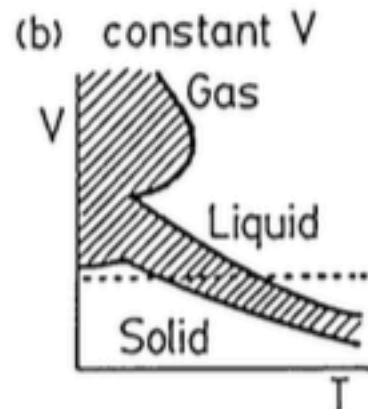
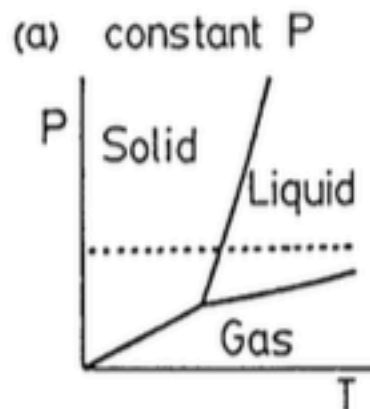


Figure 6.7: Trajectories of the harmonic oscillator: (from left to right) in the microcanonical ensemble, using the Andersen method, and using the Nosé-Hoover method. The y axis is the velocity and x axis is the position.

Constant pressure or constant volume

- At constant pressure phase transitions are sharp
- At constant volume, a two phase region (shaded region) is seen.
- In a finite cell, one will have droplets/crystallites form, but surface tension will make a barrier to the formation of them.
- An additional problem is the shape of simulation cell, that will favor certain crystal structures.



Features of Constant Pressure/Variable Structure Simulations

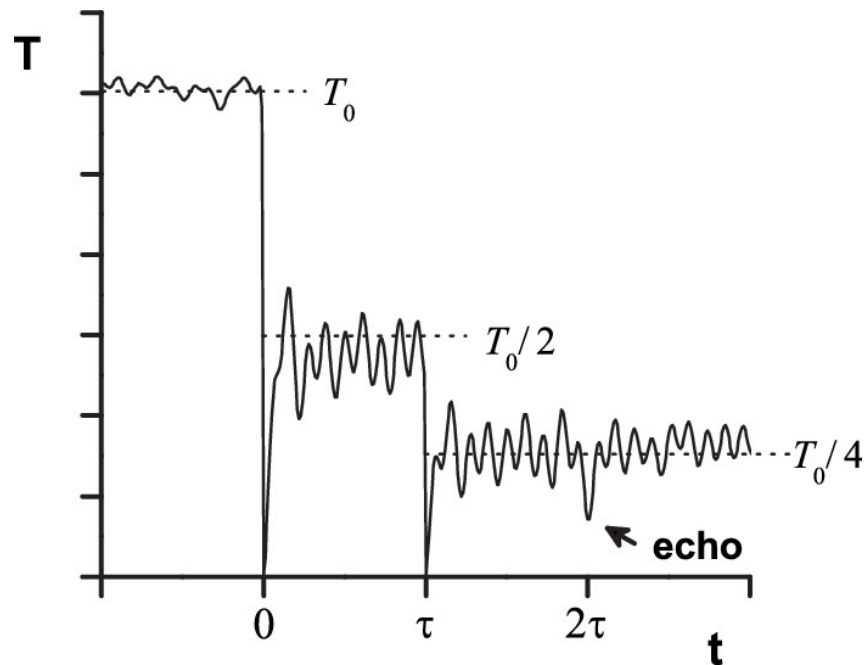
- Can “automatically” find new crystal structures
- Nice feature is that the boundaries are flexible
- But one is not guaranteed to get out of local minimum
- *One can get the wrong answer.* Careful free energy calculations are needed to establish stable structure.
- All such methods have *non-physical dynamics* since they do not respect locality of interactions but non-physical effects are small: $O(1/N)$.

REFERENCES

1. H. C. Andersen, *J. Chem. Phys.* 72, 2384 (1980).
2. M. Parrinello and A. Rahman, *J. Appl. Phys.* 52, 7158 (1981).
3. R. Martonak *Eur. Phys. J. B* 79, 241–252 (2011)

<https://carnevalelab.org/toolsmethods.html>

A note on Temperature Echo



J. Chem. Phys. 132, 114901 (2010); <https://doi.org/10.1063/1.3353952>

Dendrimers, proteins

